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Relationship between the Emission Spectra and Resonance Raman Excitation Profiles of $\mathrm{W(CO)_4}$(α-diimine) Complexes

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The photophysical properties of several $\mathrm{W(CO)_4}$(α-diimine) complexes at 293 and 80 K are reported. For complexes of the type $\mathrm{W(CO)_4L}$ (L = substituted 1,10-phenanthroline or 2,2′-bipyridine) three emissions are found while the lowest energy emission is not observed at room temperature for complexes of the type $\mathrm{W(CO)_4L}$ (L = substituted 1,4-diaza-1,3-butadiene or pyridine-2-carbaldehyde imine). The highest energy emission in all these complexes is assigned to be LF in character; the other ones appear to have MLCT character. The occurrence of the lowest energy emission, which is related to the z-polarized $b_2 \rightarrow b_2^*$ transition, depends on the MLCT character of this transition. This relationship is deduced from the resonance Raman excitation profiles and the luminescence excitation spectra of these complexes. Complexes with strong MLCT character for the z-polarized $b_2 \rightarrow b_2^*$ transition show a low-energy emission, while this is not the case for complexes with much less MLCT character for this transition. These results are explained by the efficiency of the radiationless processes, which is large when metal–ligand stretching modes act as promoting modes.

Introduction

The photochemical and photophysical behavior of transition-metal complexes possessing low-energy metal to ligand charge-transfer (MLCT) states has been the subject of many investigations during the last decade.[1]

Although luminescence has been observed for many complexes at low temperature,[2] only a few complexes appear to luminesce at room temperature. The latter phenomenon has been observed e.g. for the carbonyl d^6 complexes of the type $\mathrm{Re(CO)_3XL}$ (X = halide; L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and related ligands),[3] $\mathrm{W(CO)_5L}$ (L = substituted pyridine),[4] and quite recently $\mathrm{M(CO)_4L}$ (M = Cr, Mo, W; L = bpy, phen).[5] The last complexes even show a double emission at room temperature in solution. The spectroscopic properties of these complexes have been studied in detail in our laboratory, and special attention has been paid to the resonance Raman (RR) and magnetic circular dichroism (MCD) spectra in relation to the photosubstitution quantum yields upon excitation into the lowest MLCT band.[6]

Preliminary measurements on the room-temperature emission of the corresponding complexes $\mathrm{W(CO)_4}$(R-DAB) (R-DAB = 1,4-diaza-1,3-butadiene; R—N=CH—CH=NR) and $\mathrm{W(CO)_4}$(R-Pyca) (R-Pyca = pyridine-2-carbaldehyde imine; $\mathrm{C_5H_4N}$—CH=NR)[7] only showed a single emission. This prompted us to study in more detail the emission spectra of the complexes $\mathrm{W(CO)_4L}$ (L = 4,7-$\mathrm{Ph_2}$-phen, *i*-Pr-DAB, and *i*-Pr-Pyca) in relation to their electronic absorption, MCD, and RR spectra. The structure of the R-DAB complexes is shown in Figure 1.

Experimental Section

Preparations. All complexes were synthesized by methods described earlier[8] and were carefully purified before use. A literature procedure[9] was followed in the case of the $\mathrm{W(CO)_4}$(tmen) complex (tmen = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine). Solvents were distilled several times before use and kept under nitrogen.

Spectra. Cary 14 and Perkin-Elmer Lambda 5 spectrophotometers were used to measure the electronic absorption spectra.

The luminescence spectra as well as the resonance Raman spectra were recorded on a Jobin Yvon HG2S Ramanor instrument using a SP Model 171 $\mathrm{Ar^+}$ laser and a CR 490 tunable dye laser with Rhodamine 110, Rhodamine 6G, and Coumarin 6 as dyes. An Anaspec 300-S filter with a band-pass of 0.4 mm was used as a premonochromator. The room-temperature spectra were recorded in a spinning cell whereas measurements at low temperatures were carried out in a Cryoson Dewar cooled with liquid nitrogen. The windows of both the Dewar and the cell are made of optical quality quartz. Carefully distilled 2-Me-THF was used as the solvent for the low-temperature measurements. All experiments were performed with dry and carefully degassed solutions.

The emission maxima cited in this article are corrected for the sensitivity of the spectrophotometer. The RR intensities used for the excitation profiles were measured on a Hewlett-Packard Model 10 calculator with a 9864A digitizer and corrected for the spectrophotometer sensitivity, the decomposition in the laser beam, and the absorption of the scattered light. The tungsten tetracarbonyl complexes are quite stable in the laser beam.

The MCD spectra were recorded at the Laboratorium voor Algemene Chemie of the Rijksuniversiteit van Utrecht with a homemade instrument, consisting of a Hilger and Watts Model D 330 monochromator, a Morvue Model PEM-3 photoelastic modulator, and a PAR Model 186 synchrohet-lock-in amplifier.

Luminescence excitation spectra were measured with an Osram 450-W Xenon arc light source, which was placed in a Zeiss Lamphouse. The excitation wavelength was selected by a Zeiss M20 grating monochromator or a Zeiss MM12 quartz prism double monochromator. The emitted light from the 40 × 10 × 10 mm quartz cell was focused on a Zeiss M20 grating monochromator equipped with an EMI 9558 QA photomultiplier. The signal was amplified with a Princeton Model 1121 discriminator control unit and a Model 1109 photon counter. The luminescence excitation spectra were corrected for the output of the Xenon lamp–monochromator combination by following a literature procedure.[10]

Results and Discussion

The MO diagram of a $\mathrm{W(CO)_4}$(α-diimine) complex with C_{2v} symmetry (Figure 2) shows the presence of three allowed low-energy transitions with different polarizations from the metal d orbitals to the lowest π^* orbital of the α-diimine ligand. From these transitions the z-polarized $b_2 \rightarrow b_2^*$ transition will be the strongest one since it represents the transition between the metal d_{yz} orbital (symmetry b_2) and the lowest π^* level of the α-diimine ligand (b_2^*) which are strongly mixed in the ground and excited state. It is directed along the dipole vector of the complex (z axis,

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(7) The abbreviations R-DAB and R-Pyca in this paper, used for economy of space, imply that the α-diimine carbon atoms are protonated; e.g., *i*-Pr—N=CH—CH=N—*i*-Pr becomes *i*-Pr-DAB. Other important abbreviations for the R groups used throughout this paper are Me = methyl, Ph = phenyl, *i*-Pr = isopropyl, Mes = mesityl (van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151).

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Table I. Properties of the MLCT Band and Luminescence Characteristics for a Series of W(CO)$_4$L Complexes

complex	λ^{max}(C$_6$H$_6$),[a] nm	ϵ^{max}(C$_6$H$_6$), L mol^{-1} cm^{-1}	$10^{-3}\Delta^{max}$,[b] cm^{-1}	luminescence: $10^{-3}\lambda^{max}$(293 K),[c] cm^{-1} high energy	luminescence: $10^{-3}\lambda^{max}$(293 K),[c] cm^{-1} low energy	luminescence: $10^{-3}\lambda^{max}$(80 K),[d] cm^{-1} high energy	luminescence: $10^{-3}\lambda^{max}$(80 K),[d] cm^{-1} low energy
W(CO)$_4$(4,7-Ph$_2$-phen)	517	10 400	2.3	17.75	13.10	*e*	14.90
W(CO)$_4$(4,4′-Me$_2$-bpy)	497	5 300	2.3	17.82	13.16	*e*	15.92
W(CO)$_4$(Mes-Pyca)	570	11 300	1.7	16.23	*f*	17.36	13.14
W(CO)$_4$(*i*-Pr-Pyca)	538	9 700	2.0	17.50	*f*	17.94	13.90
W(CO)$_4$(Mes-DAB)	542	14 100	0.0	16.86	*f*	17.38, 19.57[g]	*f*
W(CO)$_4$(*i*-Pr-DAB)	532	15 400	0.9	17.37	*f*	17.79	*f*
W(CO)$_4$(tmen)	404(LF)			~18.40[h]		18.42	

[a] λ^{max} = maximum of MLCT band unless specified otherwise. [b] $\Delta^{max} = \sigma^{max}(CH_3CN) - \sigma^{max}(C_6H_6)$. [c] Measured in C$_6H_6$, excitation wavelength 488 nm. [d] Measured in 2-Me-THF, excitation wavelength 488 nm. [e] This weak band is partly obscured by the inense low-energy emission. [f] No emission is observed. [g] Highest energy emission separated. [h] Very weak emission.

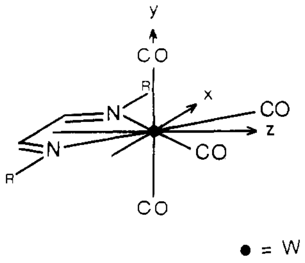

Figure 1. Structure of W(CO)$_4$(R-DAB).

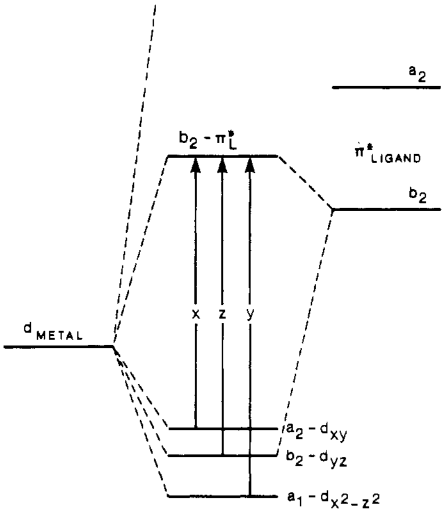

Figure 2. Relevant part of the MO diagram including the possible MLCT transitions with their polarization directions.

Figure 1), which results in a larger solvatochromism for this transition compared to the *x*- and *y*-polarized ones.

Apart from these transitions two transitions are allowed to the second π^* level of the α-diimine ligand (a_2^*), which however will not be discussed here.

The amount of mixing between the metal d_{yz} and ligand π^* orbital will depend on the energy and atomic coefficients of the π^* level. By using different ligands, one can therefore influence this degree of mixing. An increase of mixing will cause a decrease of the MLCT character and solvatochromism of the *z*-polarized transition. In the extreme case of complete mixing this electronic transition will no longer have MLCT character but instead will be a metal (d_{yz})–ligand (π^*) bonding to antibonding transition. In that case the transition will not be solvatochromic.

Electronic Absorption Spectra. All complexes of the type M(CO)$_4$(α-diimine) (M = Cr, Mo, W) show an intense absorption band in the visible region, which has been assigned to MLCT transitions.[11] The bands often show solvatochromism, in contrast with the ligand field (LF) transitions in the 350–420-nm region.

Table II. Excitation Wavelength Dependence of the Emission at 293 K in C$_6$H$_6$

complex	excitation wavelength, nm	$10^{-3}\lambda^{max}$(emission), cm^{-1} high energy	$10^{-3}\lambda^{max}$(emission), cm^{-1} low energy
W(CO)$_4$(4,7-Ph$_2$-phen)	514.5	16.6[a]	13.0
	488.0	17.8	13.1
	476.5	18.0	13.1
	457.9	18.3	13.1
W(CO)$_4$(*i*-Pr-DAB)	514.5	17.2	*b*
	488.0	17.5	*b*
	457.9	18.0	*b*

[a] Observed as a shoulder of the low-energy band. [b] No emission observed.

For some of these complexes the different transitions within this MLCT band have been assigned with the use of RR and MCD spectroscopy.[12] From these transitions the strongest one has been assigned to the *z*-polarized $b_2 \rightarrow b_2^*$ transition. In Table I the absorption data of the complexes are collected. From the difference in solvatochromism it appears that the mixing of metal d_{yz} and ligand π^* orbitals is much stronger in the R-DAB complex compared to that in the phen and bpy complexes. The MLCT character of this band in the *i*-Pr-Pyca complex is between that of the *i*-Pr-DAB and 4,7-Ph$_2$-phen complexes as is evident from the solvatochromism. It will be shown that this MLCT character of the *z*-polarized transition strongly influences the photophysical behavior of these complexes.

Luminescence Spectra. W(CO)$_4$L (L = substituted phen or bpy) complexes have been found to emit strongly at 77 K in EPA glasses.[13] This emission has been assigned to a ^{3}MLCT emission although the meaning of a spin-multiplicity label is questionable here because of the large spin–orbit coupling in these tungsten complexes. Especially for dπ^* states it has been proved that the use of a spin label is not justified.[14] Recently, Manuta and Lees[5] reported room-temperture emission for these complexes in solution and they found a double emission. Both emissions were assigned to have MLCT character, the lower energy one because of its solvent dependence. For the higher energy emission LF character was rejected since no such emission was observed at room temperature for the corresponding W(CO)$_4$(en) (en = ethylenediamine) complex. This complex has no low-lying MLCT states but LF states at nearly the same energy as those of the W(CO)$_4$(α-diimine) complexes.

We have measured the luminescence spectra of the *i*-Pr-DAB and *i*-Pr-Pyca complexes in comparison to those of the 4,7-Ph$_2$-phen and 4,4′-Me$_2$-bpy complexes, and some results are shown in Figure 3 and Table I. The most remarkable result is the complete absence of the low-energy emission at 293 K for the *i*-Pr-DAB and *i*-Pr-Pyca complexes. Both emission bands of the

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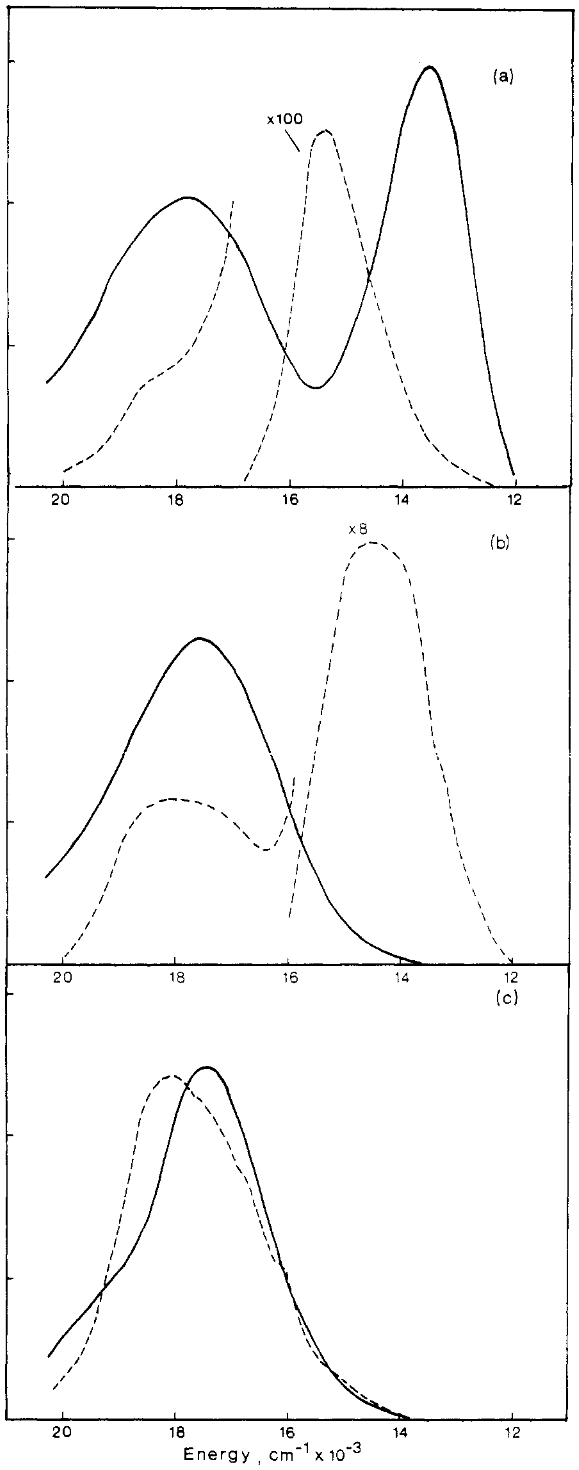

Figure 3. Luminescence spectra at 293 K in C_6H_6 (—) and at 80 K in 2-Me-THF (---) of (a) $W(CO)_4$(4,7-Ph_2-phen), (b) $W(CO)_4$(*i*-Pr-Pyca), and (c) $W(CO)_4$(*i*-Pr-DAB). The excitation wavelength is 488 nm.

4,7-Ph_2-phen and 4,4′-Me_2-bpy complexes as well as the single, high-energy emission band of the *i*-Pr-DAB and *i*-Pr-Pyca complexes are solvent dependent, which supports the MLCT character of these emissions.

The excitation wavelength dependence of the emissions was also investigated (Table II) in order to confirm the presence of two emissions in the case of the substituted phen and bpy complexes and of only one for the R-DAB and R-Pyca complexes. However, irradiation with different laser frequencies caused an unexpected shift of the position of the common high-energy emission of these complexes. It shifted to higher energy upon higher frequency excitation, which points to the presence of at least two emissions within this high-energy emission band. In the case of $W(CO)_4$(*i*-Pr-DAB) nearly two separated bands were found upon excitation with λ = 458 nm. The occurrence of this "third" emission in other solvents as well rules out the possibility of an emission of the solvent itself or of any impurity in the solvent. Moreover, the intensity of this emission increases upon higher energy excitation and its position is not solvent dependent, results which point to a LF emission. We therefore also studied the emission of $W(CO)_4$(tmen) (tmen = *N,N,N′,N′*-tetramethylethylenediamine), for which complex no MLCT emissions are expected (vide supra).

$W(CO)_4$(en) has been found to emit from its lowest ^{3}LF state at 77 K (maximum at 545 nm[13]). A similar ^{3}LF emission is found for $W(CO)_4$(tmen) both at room temperature (very weak, Table I) and at 80 K in a 2-Me-THF glass (Table I), which is in good agreement with the highest energy ("third") emission of the $W(CO)_4$(α-diimine) complexes.

Emission data of the complexes at 80 K in a 2-Me-THF glass are also given in Table I and Figure 3. Again, there are remarkable differences between the luminescence behavior of the different types of α-diimine complexes. The low-energy emission of $W(CO)_4$(4,7-Ph_2-phen) shifts to higher energy below the glass point of 2-Me-THF (130 K), and its intensity increases enormously. The other emission band is then still present as a shoulder but nearly as weak as in the room-temperature spectrum (Figure 3a).

This shift of the low-energy emission on cooling to 80 K has also been observed by Wrighton and co-workers[3] for the complexes $Re(CO)_3XL$ (X = halide; L = phen and bpy ligands). It has been ascribed to a so-called "rigidochromic" effect, the origin of which is not yet fully understood.

The intensity ratio of the two emission bands hardly changes upon cooling to the glass point, which means that there is no thermal equilibrium between the two emitting states in solution. The MLCT emission of the R-DAB complexes increases only a little when 2-Me-THF becomes a glass and only shows a minor shift to higher energy (Figure 3c). The R-Pyca complexes however show a low-energy emission in the glass which is not present in the room-temperature spectra (Figure 3b). So the 80 K emission of the R-Pyca complexes resembles that of the substituted phen and bpy complexes while the room-temperature emission is nearly the same as that of the R-DAB complexes. This intermediate behavior of the R-Pyca complexes, which is also reflected in their photochemical behavior,[15] can be understood from the excited-state properties of these compounds, which have been studied by RR spectroscopy (vide infra).

At 80 K the same wavelength dependence for the high-energy MLCT emission was found for the R-DAB complexes as at room temperature, whereas for the other complexes these measurements were hindered by the intense low-energy emission.

Furthermore, the position of the highest energy component of the $W(CO)_4$(Mes-DAB) emission (separated upon 458-nm excitation) nearly coincided with the ^{3}LF emission of $W(CO)_4$(tmen). We therefore assign this "third" emission for all α-diimine complexes to a ^{3}LF emission.

Resonance Raman Excitation Profiles. RR spectra have proved to give valuable information about the character of allowed electronic transitions and the properties of excited states.[16] Moreover, with the use of RR excitation profiles different electronic transitions within one absorption band can be visualized and assigned. We have applied this technique to complexes of the type $M(CO)_4$(R-DAB) (M = Mo, W) and $Re(CO)_3X$(R-DAB) (X = halide),[17] and the RR spectra of these complexes

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appeared to change dramatically when the MLCT character of the electronic transitions varied. A decrease of MLCT character due to an increase of metal to α-diimine π back-bonding caused a decrease of the RR intensity of the ligand stretching modes and an intensity increase of the metal–ligand stretching and ligand bending modes. Besides, a decrease of MLCT character appeared to be accompanied by a decrease of the luminescence quantum yield.

In order to get more insight into the observed photophysical behavior of such complexes compared to the MLCT character of their electronic transitions, we studied in more detail the RR excitation profiles of three representative complexes of the type W(CO)$_4$L (L = 4,7-Ph$_2$-phen, *i*-Pr-DAB, and *i*-Pr-Pyca) (Figure 4). The RR spectra of W(CO)$_4$(4,7-Ph$_2$-phen) show, throughout the main absorption band, strong resonance enhancement for the symmetrical ligand stretching modes as well as for $\nu_s(\mathrm{CO}^{\mathrm{cis}})$, the symmetrical stretching mode of the carbonyls in the cis position with respect to the α-diimine ligand. The metal–ligand stretching modes, on the other hand, are weak, and ν_s(W–N) can hardly be detected. The strong RR effect observed for the ligand stretching modes implies that during these electronic transitions much charge is transferred to the α-diimine ligand. From the weak RR effect of ν_s(W–N) it can be concluded that this transfer of charge hardly affects the metal–ligand bond strength.

The RR spectra of W(CO)$_4$(*i*-Pr-DAB) show different features. Upon excitation at the high-energy side of the absorption band strong resonance enhancement is observed for ν_s(CN), the symmetrical stretching mode of the C═N bonds, and for $\nu_s(\mathrm{CO}^{\mathrm{cis}})$. However, upon excitation at the low-energy side of the absorption band the metal–ligand stretching modes are the most intense. This behavior is clearly shown in the excitation profiles for ν_s(CN) (1482 cm^{-1}) and ν_s(W–N) (230 cm^{-1}). Only one maximum is found for ν_s(CN) at 520 nm, which means that this transition, which is also present at 515 nm in the excitation profiles of W(CO)$_4$(4,7-Ph$_2$-phen), has MLCT character in both complexes. On the other hand, the maximum in the excitation profile for ν_s(W–N) at 550 nm (for ν_s(CN) not even a shoulder is found at this wavelength) corresponds to a transition that has no MLCT character but that is instead strongly metal–ligand bonding to metal–ligand antibonding. This maximum and the corresponding one at 535 nm in the excitation profiles of the 4,7-Ph$_2$-phen complex apparently belongs to the *z*-polarized $b_2 \rightarrow b_2^*$ transition. In contrast with the *i*-Pr-DAB complex the excitation profile of the ligand stretching mode ν(phen II)[6] (1555 cm^{-1}) for the 4,7-Ph$_2$-phen complex also shows a maximum at 535 nm, which is in agreement with the stronger MLCT character of the $b_2 \rightarrow b_2^*$ transition in this complex.

The shoulder in the excitation profile for ν_s(W–N) of the *i*-Pr-DAB complex at ~560 nm is more pronounced in the excitation profile for this vibration of the *i*-Pr-Pyca complex (see Figure 4c). It is assigned to the *x*-polarized $a_2 \rightarrow b_2^*$ transition since resonance enhancement of ν_s(W–N) is mainly expected for electronic transitions within the *xz* plane of the complexes.

Finally, the maximum discussed before, which is observed at 515 nm for the 4,7-Ph$_2$-phen complex, at 520 nm for the *i*-Pr-DAB complex, and at 525 nm for the *i*-Pr-Pyca complex, is assigned to the *y*-polarized $a_1 \rightarrow b_2^*$ transition. All three complexes show strong MLCT character for this transition while only a minor RR effect is observed here for the metal–ligand stretching modes. It appears from Figure 4 that the *z*-polarized transition of the *i*-Pr-Pyca complex has an intermediate MLCT character (there is no distinct maximum for ν(py II)[6] at 550 nm). This can be expected from the energy of the lowest π^* orbital of this ligand with respect to the corresponding orbitals of the 4,7-Ph$_2$-phen and *i*-Pr-DAB ligands.[18]

It should be noticed that in these complexes only three MLCT transitions are found in the excitation profiles. A fourth transition, which is present in the excitation profiles of the corresponding Mo(CO)$_4$(α-diimine) complexes at the high-energy side of the

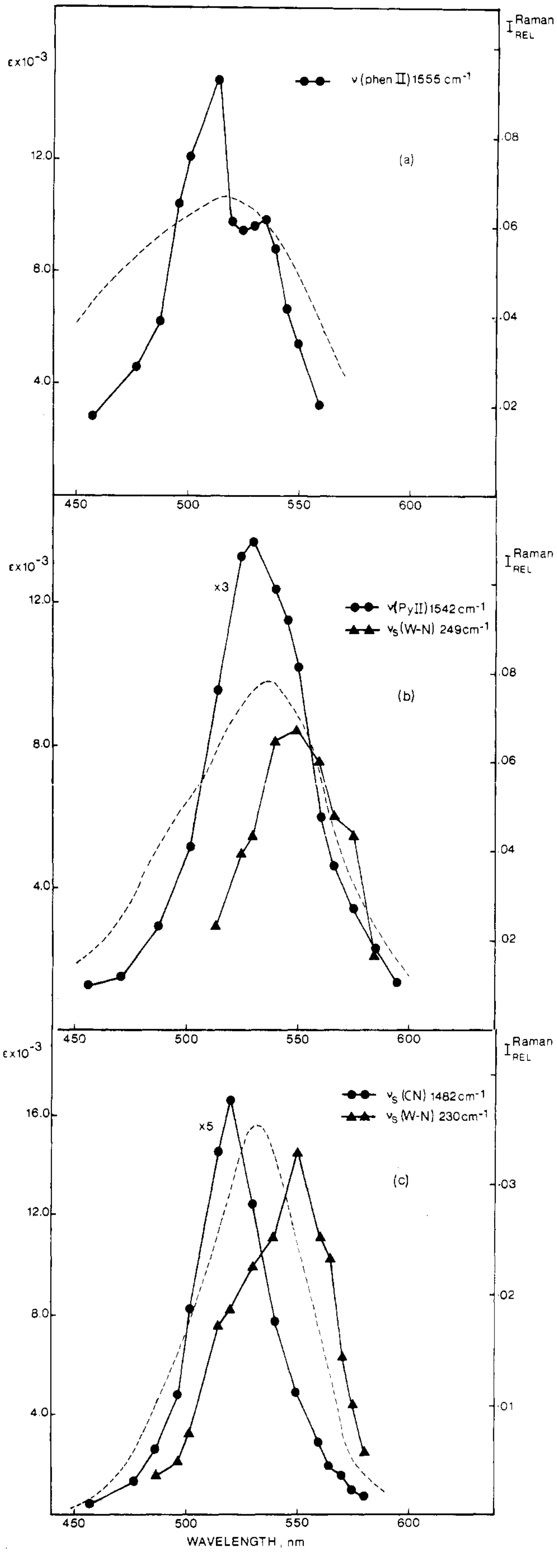

Figure 4. Excitation profiles in C$_6$H$_6$ of (a) W(CO)$_4$(4,7-Ph$_2$-phen), (b) W(CO)$_4$(*i*-Pr-Pyca), and (c) W(CO)$_4$(*i*-Pr-DAB) relative to the 992-cm^{-1} band of C$_6$H$_6$.

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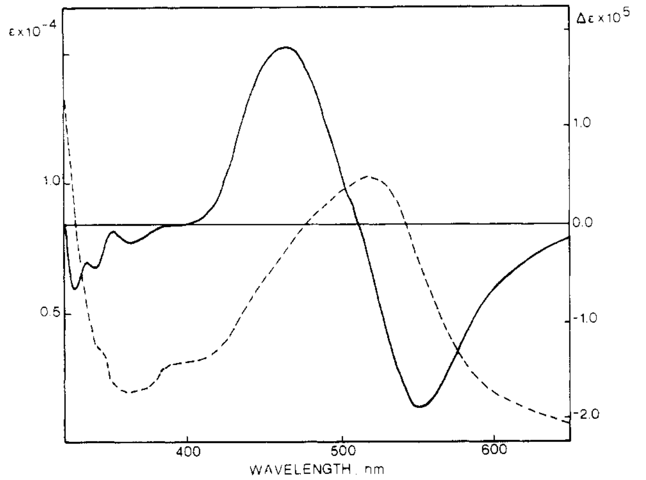

Figure 5. MCD (—) and electronic absorption (---) spectra of W(CO)$_4$(4,7-Ph$_2$-phen) in C$_6$H$_6$.

MLCT absorption band,[17] is not found for the W(CO)$_4$(α-diimine) complexes. It is however observed in the MCD spectrum of W(CO)$_4$(4,7-Ph$_2$-phen) (Figure 5) at 470 nm and is tentatively assigned to the $a_2 \rightarrow a_2^*$ transition from the metal $d_{xy}(a_2)$ orbital to the second $\pi^*(a_2)$ level of the ligand. The absence of this transition in the excitation profiles is most likely due to a deenhancement of Raman intensity for this transition caused by the ^{3}LF transition. These effects have been discussed by Stein et al.[19] The MCD spectrum of W(CO)$_4$(4,7-Ph$_2$-phen) shows a negative *B* term for the transition mentioned above while another strong positive *B* term is found at 550 nm, which nearly coincides with the *z*-polarized MLCT transition in the excitation profiles. It should be noticed that the maxima of the excitation profiles do not completely coincide with the *B* term because of interference between amplitudes of preresonant and more nearly resonant states.[20]

The excitation profiles have shown that in particular the MLCT character of the *z*-polarized transition is influenced by variation of the α-diimine ligand. For the *i*-Pr-DAB complex no MLCT character is found for this transition whereas the transition of the 4,7-Ph$_2$-phen complex has much MLCT character. In order to find out whether this difference in MLCT character is responsible for the presence or absence of the low-energy emission, luminescence excitation spectra have been recorded.

Luminescence Excitation Spectra. For W(CO)$_4$(4,7-Ph$_2$-phen) luminescence excitation spectra at room temperature have been measured at different detection wavelengths. However, only the spectrum obtained upon detection at 730 nm, close to the maximum of the low-energy emission, gave reliable results since the high-energy emission appeared to be too weak for this technique. The same holds for the weak emission of the W(CO)$_4$(*i*-Pr-DAB) and W(CO)$_4$(*i*-Pr-Pyca) complexes. Therefore, only the origin of the low-energy emission of the W(CO)$_4$(4,7-Ph$_2$-phen) complex is discussed here. Figure 6 shows that in particular the transition at 530 nm, which corresponds with the *z*-polarized $b_2 \rightarrow b_2^*$ transition, contributes to the low-energy emission. Excitation spectra measured in other solvents show that the transition mainly responsible for this emission is highly solvatochromic. This is also in agreement with a MLCT emission from a level related to the *z*-polarized $b_2 \rightarrow b_2^*$ transition. This level is also populated from at least one higher MLCT level since a shoulder in the excitation spectrum is observed at 470 nm, which has been assigned to the $a_2 \rightarrow a_2^*$ transition (vide supra).

A similar spectrum is obtained for the lowest energy emission of W(CO)$_4$(4,4′-Me$_2$-bpy). These spectra clearly show that the low-energy emission mainly originates from the *z*-polarized $b_2 \rightarrow b_2^*$ transition. The decrease of MLCT character of this transition on going from the 4,7-Ph$_2$-phen to the *i*-Pr-DAB and *i*-Pr-Pyca complexes, which was evident from the RR spectra, apparently leads to the disappearance of this emission. This behavior can be explained by the efficiency of the nonradiative processes in these complexes. In the case of the R-DAB complexes only metal–ligand vibrations are affected during the *z*-polarized transition while internal vibrations of the α-diimine ligand are affected during this transition in the substituted phen and bpy complexes. For the radiationless transitions therefore the ligand vibrations will act as promoting modes in the latter complexes while in the R-DAB complexes this is the case for the metal–ligand vibrations.

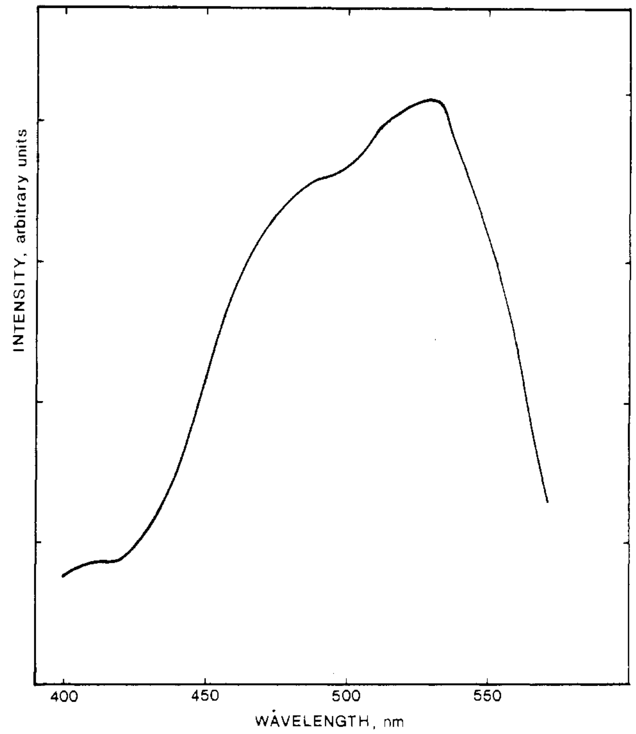

Figure 6. Luminescence excitation spectrum of W(CO)$_4$(4,7-Ph$_2$-phen) in C$_6$H$_6$ detected at 730 nm.

Interesting work on radiationless processes in transition-metal complexes by Robbins and Thomson[21] has shown that the electronic integral $J_k(m,n)$, which is part of the matrix element connecting ground and excited states, is largest when the promoting mode *k* belongs to metal–ligand skeletal vibrations. As a result, if in a complex these vibrations can act as promoting modes, effective radiationless relaxation is expected, thereby reducing the luminescence quantum yield. These results for the tungsten complexes are in good agreement with this theory, viz. efficient radiationless processes in the R-DAB complexes resulting in the absence of the low-energy emission.

At room temperature the R-Pyca complexes act like the R-DAB complexes, although the *z*-polarized $b_2 \rightarrow b_2^*$ transition has some MLCT character according to the RR excitation profiles. At low temperatures in the rigid medium however, where nonradiative processes are less effective, the emission becomes competitive for the R-Pyca complexes.

Conclusion

The results of this study clearly show that resonance Raman excitation profiles can be used to explain the photophysical properties of complexes.

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